Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.9 No.3, 2017
www.iiste.org

Effects of Physical Activation Procedure on the Production Yield, Surface Chemistry and Surface Pores of Coconut Shells Based Activated Carbons

John. Bentil[1]* William Kwame Buah[2]
1.Department of Civil Engineering, Takoradi Polytechnic, Ghana, P.O.Box 256, Takoradi, Ghana.
2.Department of Minerals Engineering, University of Mines and Technology, Tarkwa, Ghana

Abstract
Activated carbons are produced either by physical or chemical activation or both. However, due to different experimental protocols used in preparing and characterising these carbons, it has been difficult in comparing their yields, surface chemistry and pore developments. In this study the effects of physical activation procedure on yields, surface chemistry and surface pore developments of activated carbons prepared by three physical activation procedures using the same protocols were compared. The results of the yields revealed that during the production of activated carbons better yields are obtained when the particle size of the precursor is reduced to the required size of the expected activated carbon prior to carbonisation and activation. The spectra produced by Fourier transmission infrared spectroscopy demonstrated shift in bands and changes in wavelength numbers and absorbance between the raw and the derived activated carbons during pyrolysis or activation. Comparing the micrographs of the Scanning electron microscope of the derived carbons also showed an irregular and heterogeneous surface morphology with a well-developed porous structure.
Keywords: porosity, micrographs, surface area, yield, activation, spectroscopy

1.0 Introduction

Activated carbons (ACs) are carbonaceous materials with high developed porosity, large surface area, variable surface chemistry characteristics and a high degree of surface reactivity. These unique characteristics of ACs make ACs very versatile adsorbents (Dias *et al*., 2007). ACs are largely and increasingly used in the removal of organic chemicals and metal ions of environmental or economic concerns in potable water, industrial effluents and waste water (Bentil and Buah, 2016; El-Hendawy, 2003; Afrane and Owusu-Achaw, 2008). These and other uses of ACs have made them materials of scientific and engineering investigations, and more expensive than other adsorbents due to the high production cost.

ACs are conventionally prepared either by physical or chemical activation processes or both (Yeganeh *et al*., 2006;Lillo-Rodenas *et al*., 2007). Current studies on physical activation performance have centred on the activation of lignocelluloses and other waste materials. Their advantages as carbon feedstocks include availability as renewable resources, low ash content, reasonable hardness, and their ability to produce granular activated carbons. Coconut shells were selected for this study among the agricultural by-products due to the considerable amount generated in Ghana. Coconut shells are generated during the extraction of oil coconut, and the coconut kernel separated from the shell. It was estimated that 170.64 x 1000 tonnes of this agricultural residue was generated in the year 2008 in Ghana, and this was projected to increase in the subsequent years (Quartey and Chylkova, 2013). Small percentages are used as processing fuel while a greater percentage is wasted. Coconut shells are reported to have a less amount of ash, more amount of volatile matter and available with little or no cost in rural areas during all seasons of the year. Its high fixed carbon content leads to the usage of the char obtained after pyrolysis as an activated carbon (Afrane and Owusu-Achaw, 2008). The use of commercial ACs is not suitable to the developing countries because of their low availability and high cost. Therefore, there is a need for a practicable method to produce AC from cheaper and readily available material like coconut shell that can be economically viable in large scale and give comparable adsorbing capacity.

Notwithstanding the significant results of earlier studies on the performances of ACs during applications, there is a growing interest to research into ways to reduce the cost of ACs production by either choosing a cheap raw material or by applying a proper production method. Previous studies on activated carbons derived from lignocelluloses and waste materials have established their satisfactory performance as low cost adsorbents. It is also already established that the porosity development of activated carbons depends partly on the pore structure and the chemical composition of the parent material as well as the method used in activation process (Afrane and Owusu-Achaw, 2008). More so, the adsorption and transport behaviour of activated carbons and hence its adsorptive performance in applications like separation, purification, extraction and other areas also depend mainly on the nature and extent of the porosity of the activated carbons, which are controlled by the manufacture process. Depending on the type of precursor, the nature and conditions of the activating process, the properties of the ACs can be varied (Selomulya *et al*., 1999).

ACs as already stated, are produced by either physical or chemical activations or both. The physical

activation is the most widely used method and its performance on different precursors has been analysed carefully in literature. For instance, Hwang *et al* (2008) extracted high capacity disordered carbons from coconut shells as anode materials for lithium batteries. In 2008, Afrane and Owusu-Achaw and Gratuito *et al*., (2008) also produced activated carbons from coconut shells using physical methods. Mohan *et al*., (2008) is reported to have studied waste water treatment by low cost activated carbons derived from coconut shells and coconut fibres. Amudan *et al.*, (2007) also reported the production of a highly effective adsorbent material from the coconut shell combined with aquatic waste for the removal of heavy metals from industrial waste water. Micro porous Activated carbons were also prepared from raw coconut shells by Wei Su *et al*., in 2006.

But all these earlier studies have not made it easier to conveniently compare the surface chemistry and pore characteristics of activated carbons since different experimental protocols are used in the preparation and activation processes. Relevant comparisms can only be possible if the same experimental conditions are used for a given raw material in terms of preparation, activation and characterisation. In the present study, the effects of the same physical activation protocols on the yield, surface chemistry and pore size developments of coconut shell based activated carbons were compared for the first time. It is expected that such a study will increase existing knowledge on the mode of porosity developments and help enhance understanding of the dynamics of the surface chemistry brought about by the physical activation procedure for specific applications.

2.0 Experimental Methods

Materials

Coconuts shells were obtained from Kajeibiri, a suburb of Sekondi-Takoradi in the Western Region of Ghana. Coconuts shells are untapped resources left as waste after the fruit-pulp has been removed from coconut fruits.

Preparation of Activated Carbons

Prior to use, the coconut shells (CNT) were crushed and sieved to obtain particle sizes between 1-10mm. Subsequently, the reduced coconut shells were loaded in a gas fed pyrolysis-gasification reactor to produce activated carbons according to the procedures detailed in the Figure 1 below. The first step in activating is to carbonise the shells to drive out the volatiles out of the shells to create carbonaceous mass full of tiny pores at 900 ^{o}C. This carbonised base material in the second stage is activated at a temperature of 900 ^{o} C under the flow of steam at 10mL/min for 2 hrs. The temperature of the reactor was measured using a k-type thermocouple. Ultimate analysis was carried out using PerkinElmer CHNS/O elemental analyser. Elements covered in the analysis are carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O).Proximate analysis with the aid of Thermogravimetry Analyser was used to determine the moisture, volatile matter (VM), fixed carbon (FC), and ash content. The yields of the resulting three different activated carbons (CNP1, CNP2, and CNP3) were determined. Scanning Electron Microscope was used to determine the surface morphology and pore development, whilst a Fourier Transmission Infrared spectroscopy in the range of 400-4000cm^{-1} was also used to examine the surface chemistry (functional groups).

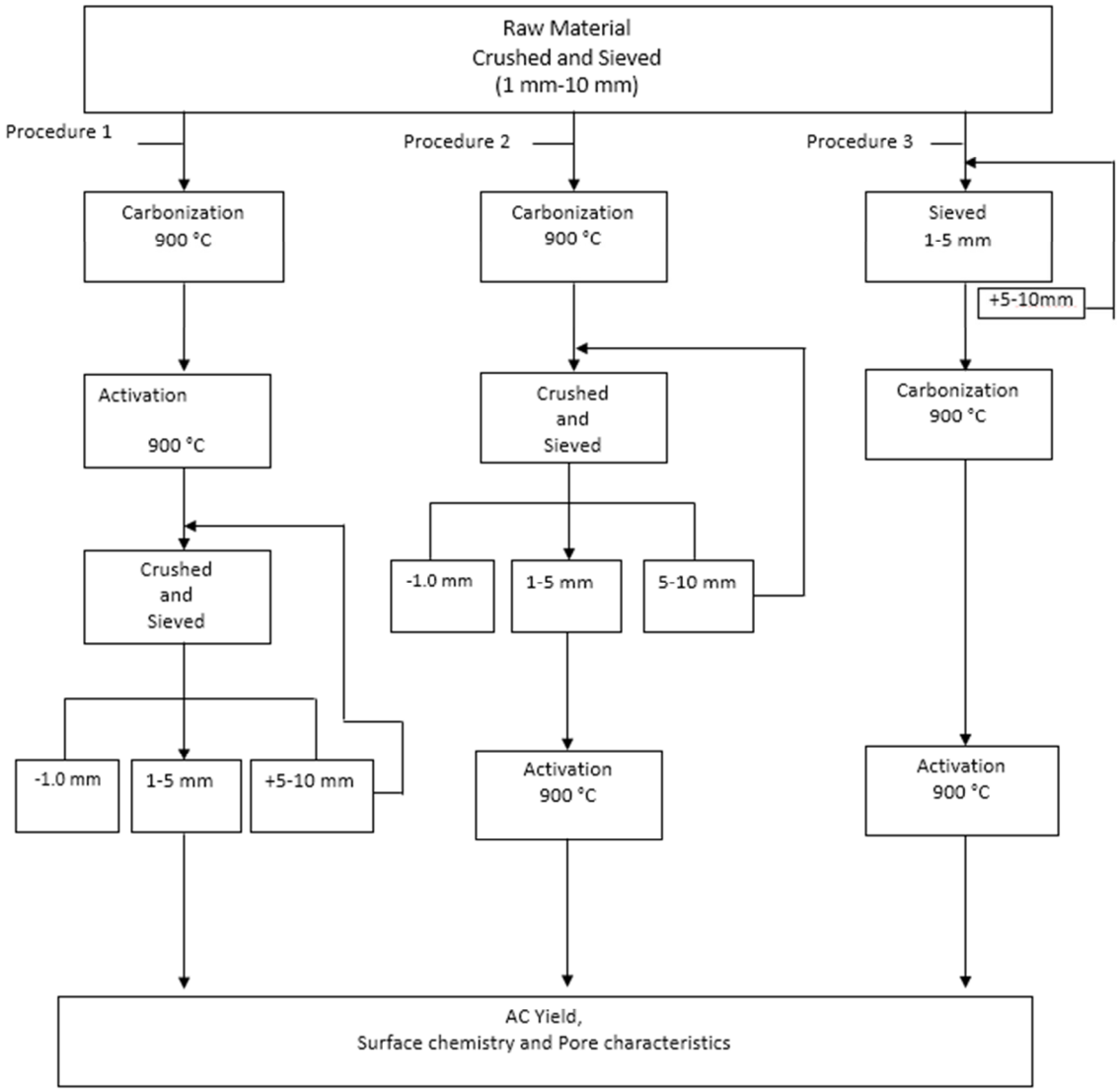

Figure 1: Flow sheet for the three production procedures

3.0 Results and Discussions

3.1 Proximate analysis of coconut shells (CNT)

Table 1: Proximate analysis of coconut shells (CNT)

Volatiles	Moisture	Fixed carbon	Ash
68.15%	5.40%	26.15%	0.30%

Table 2: Ultimate analysis of the raw coconut shells (CNT) and the derived activated carbons (CNP1, CNP2 and CNP3)

Sample	Carbon	Hydrogen	Nitrogen	Oxygen	Sulphur
CNT	43.65	5.65	4.40	45.75	0.75
CNP1	72.97	2.76	0.40	23.66	0.25
CNP2	76.98	2.51	0.36	19.94	0.21
CNP3	83.68	2.43	0.35	13.34	0.20

The results of the proximate analysis of the coconut shells are indicated in Table 1.The results are compared with previous research on coconut shell. The fixed carbon, volatiles, moisture and ash content for the coconut shells are 26.15, 68.15, 5.57 and 0.13% respectively. The high volatile matter (68.15%) and the moderate amount of fixed carbon (26.15%) is a typical property of agricultural residue (Omar *et al*., 2011). The results of the proximate analysis are within the range of literature values (Table 1). The high volatile contents make it more reactive and therefore aid during the carbonisation process in creating more pores on the carbonaceous material.

The ultimate analysis of the coconut shell indicated a carbon, hydrogen, nitrogen, sulphur and oxygen content of 43.45%, 5.65%, 4.40%. 0.75% and 45.75% respectively. The low nitrogen and sulphur content from the analysis indicates that CNT is environmentally friendly.

3.2 Activated Carbon Yield

The activated carbon yield was calculated based on the following equation:

Yield (ÿ) = (W_c/W_o) x 100 %

Where W_c (g) is the dry weight of the final activated carbon and W_o (g) is the dry weight of precursor.

Table 3: Activated Carbon Yields from the three Production Procedures

Production method	Yield %		
	Run 1	Run 2	Average
Procedure 1	15.57	14.63	15.10
Procedure 2	13.44	12.64	13.04
Procedure 3	25.19	25.26	25.23

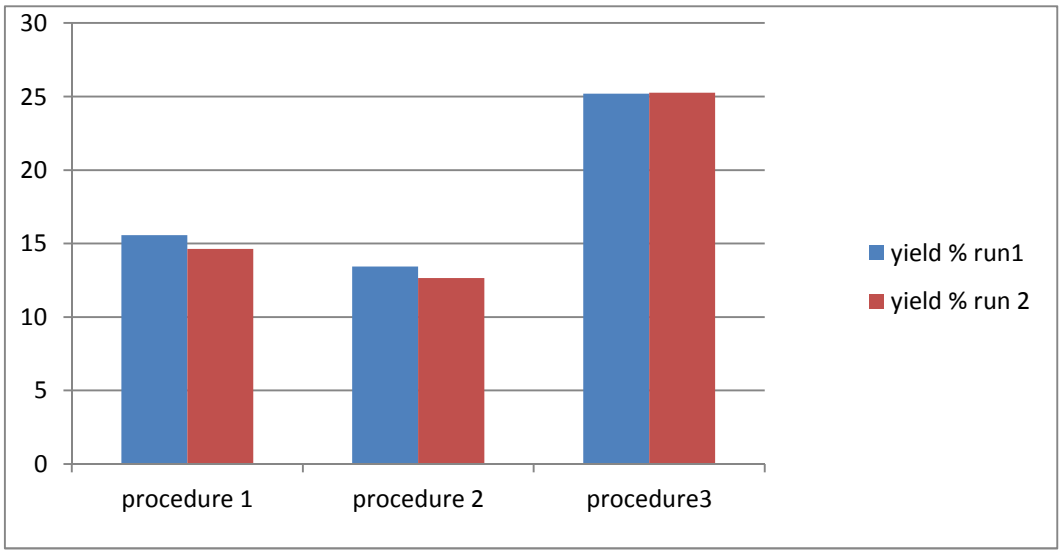

Fig.2: The activated carbon production yields by the three procedures.

It can be seen that the production yield in the procedure 3 gave the highest yield of 25.23%, followed by the procedure1 and then procedure 2, which also gave production yields of 15.10% and 13.04% respectively. Only procedure 3 have yield almost equivalent to the yield of the Thermogravimetric (TGA) proximate analysis fixed carbon yield as indicated in Tables 1 and 2. But the yields of production procedures 1 and 2 are at variance with the TGA proximate analysis value. These suggest that, during the production of ACs better yields are obtained if the particle size of the precursor is reduced to the required size of the expected activated carbon prior to carbonisation and activation. The lost of fine particles of the ACs due to further crushing to obtained the particle sizes of 1-5mm after activation may have accounted for the lower yields in the procedures 1 and 2. Shalaby *et al*, (2006) also examined the effect of the particle size of apricot stones on the properties of carbon produced, and reported that the finer the particles of the precursor, the larger the resulting yield. Muller, (2013) attributed these to the higher loss of volatile matter when particles sizes decreases.

Cagnon *et al*., (2009) reported that the three basic components of coconut shells (cellulose, hemicelluloses and lignin) under carbonisation and in terms of mass production behave like isolated. These authors stated that the structural arrangement and chemical bonds within a precursor as well as the presence of particular residue induces significant increase in weight loss under carbonisation. It could be inferred from these that the bonds within the precursor with smaller particle size are stronger than the larger ones which makes it easier to decompose the inter-particles bonds within the larger ones increasing the amount of volatile matter and increased the C-H_2O reactions; subsequently increasing the weight loss, resulting in smaller yields for the procedures 1 and 2.

3.3 Surface Chemistry Characterisation

Surface functional groups present on the surface of activated carbon mainly affect their hydrophobic / hydrophilic and acid and basic character, as a result ACs applications are conditioned by their surface chemical characteristics.

Analysis of the precursor and the derived activated carbons by Fourier transmission infrared

spectroscopy (FTIR) was performed to determine the changes in the surface chemistry of the samples and is given in Figure 3. The raw coconut shell (CNT) showed five major absorption bands at 2950-3338 cm^{-1}, 1505-1595 cm^{-1}, 1237-1421 cm^{-1}, 1000-1162 cm^{-1} and 450-770 cm^{-1}. The band at 3338 cm^{-1} is attributed to the absorption of water molecules as a result of the stretching mode of hydroxyl groups and adsorbed water, while the band at 2950 is attributed to C-H interaction with the surface of the carbon. All the three derived activated carbons spectra showed four major absorption bands. These indicate that only minor differences between the samples could be established. However, shift in bands and changes in wavelength numbers and absorbance between the raw and the derived activated carbons indicate that chemical transformation would have taken place during pyrolysis or activation as a result of decomposition of volatile matter and loss of moisture (Table 1). .

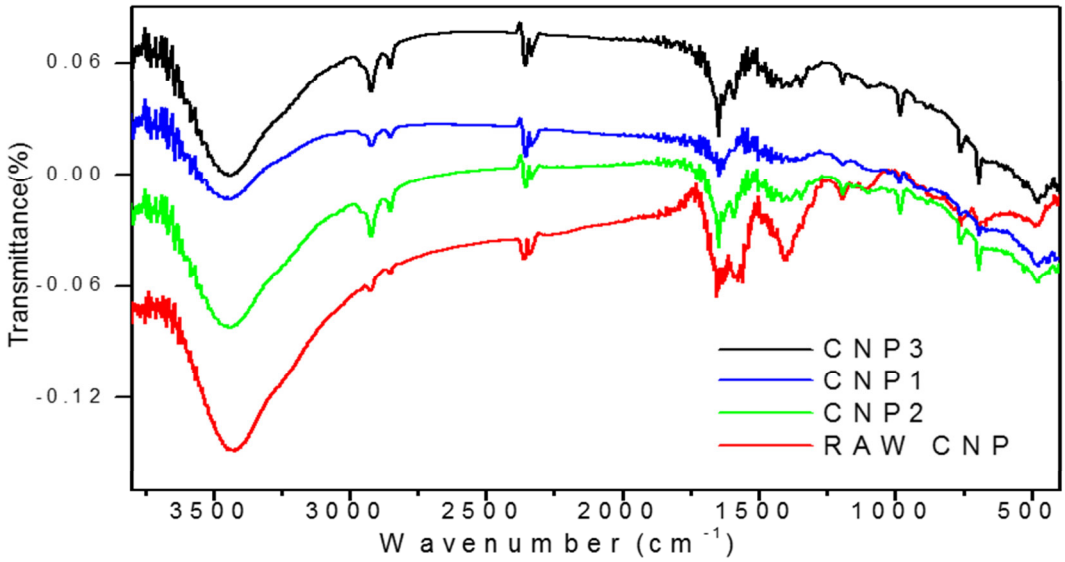

Fig.4: FTIR spectra of the raw coconut shell (CNP) and the derived activated carbons (CNP1, CNP2 and CNP3)

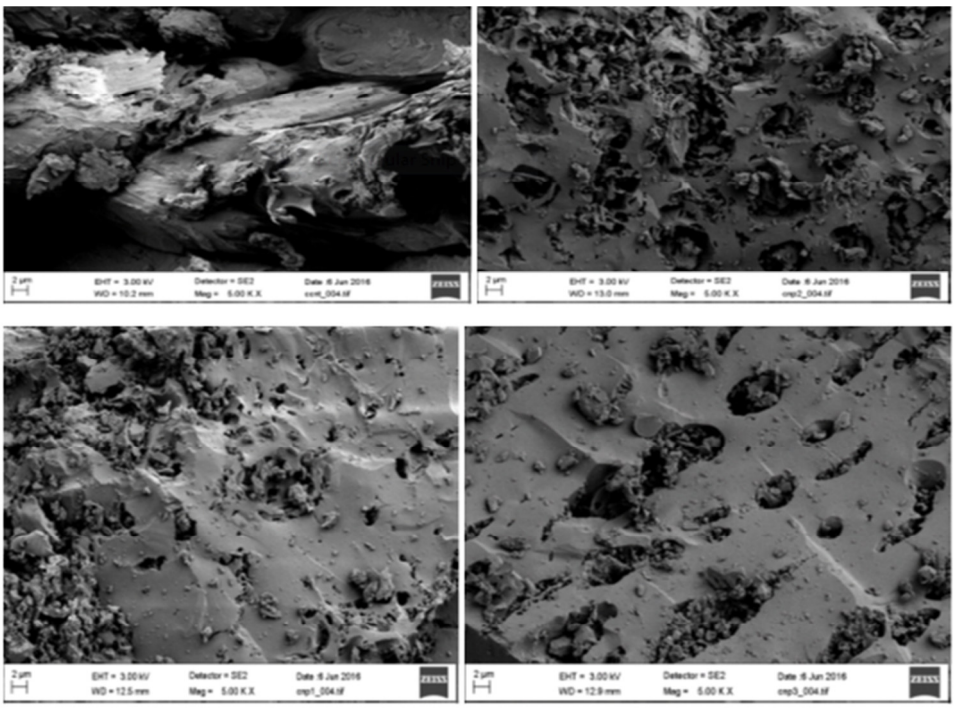

Fig 5: SEM Micrographs of the raw coconut shell and the three derived activated carbons

3.4 Surface Pores Characterisation

Activated carbon pores are divided into three major groups based on their diameter; the micropores (diameter less than 2 nm), mesopores (diameter in the range of 20-50 nm) and the macro pores (diameters greater than 50 nm). The micropore contributes to about 95% of the surface area of activated carbons and therefore determines

its adsorptive capacity (Inagaki, 2009). The textural properties of the ACs were analysed by nitrogen adsorption. The BET surface area and porosity results of the derived ACs from the three production procedures (CNP1, CNP2 and CNP3) are shown in Table 4. This indicates that the increase in both surface area and pore volume for the three activated carbons are in the order: CNP3 > CNP2 > CNP1.

Table 4: BET Analysis (Textural Property Analysis)

Sample	Surface Area m^2/g	V_{micro} Pore Size (nm)	Pore volume cm^3/g
CNP1	170.5	1.61	0.131
CNP2	207.94	1.61	0.137
CNP3	236.9	1.61	0.162

Scanning electron microscope (SEM) was used to study the surface morphology and pore sizes of the derived activated carbons.SEM images of the raw coconut shells and obtained ACs samples are shown in Figure 5. It can be observed that the raw coconut shell shows a cellular structure that is typical of lignocellulosic materials (Fig .5a) Comparing, all the images showed an irregular and heterogeneous surface morphology with a well-developed porous structure, predominantly micro pores. Widening of pore diameters and creating of new ones is achieved after activation of the samples (Hu et al., 2001). Also, it can be observed from the micrographs that some components interfered with the surface of the ACs and reduce the development of pores. Thus, some grains in various sizes in large holes –pores of different sizes and shapes could be observed. These may be as result of the presence of potassium and other inherent minerals of the precursor; according to Afrane and Owusu-Achaw, (2008); who studied and reported that the iodine adsorption characteristics of activated carbons derived from coconut shells from five different geographical locations in Ghana showed a definite relationship to the levels of potassium and other mineral elements in the precursor shells.

4.0 Conclusion

Coconut shells were employed as the precursor for the production of activated carbons by physical activation. The yields for the different particle size ranges demonstrate that in the production of activated carbons, high production yield will only be obtained when the precursor is reduced to the desired particle size ranges before carbonisation and activation. The FTIR analysis also show that reducing the size of precursor to the desired particle sizes of the resulting ACs by physical activation lessen the destruction of the surface chemistry (functional groups) which depicts the adsorption capacity of the ACs. It was also observed from the SEM micrographs that the resulting effects of physical activation on the surface pores of coconut shells ACs are well developed pore distribution, with irregular and heterogeneous surfaces.

References

[1]. Achaw, O.-W., & Afrane, G. The evolution of the pore structure of coconut shells during the preparation of coconut shell-based activated carbons. *Microporous and Mesoporous materials* , 284-290. (2008).

[2]. Amudan, O.S., Giwa, A.A. and Bello, I.A., "Removal of Heavy Metal from Industrial Wastewater using Modified Activated Coconut Shell Carbon," Biochemical Engineering Journal, Vol. 36, pp. 174-181. (2007).

[3]. Bentil, J., & Buah, W. K. Removal of fluoride in water using activated carbons prepared fromm selected agricultural waste materials. *J. of Environment and Earth Science* , vol,6 no.4 146-152. , (2016).

[4]. Cagnon, B., Py X., Guillet A., Stoeckli F., Chambat, G., Contribution of hemicelluloses, cellulose and lignin to the mass and the porous properties of chars and steam activated carbons from various lignocellulosic precursors. Bioresource Technol. 100(1)pp. 292-298(2009).

[5]. Dias, J. M., Alvim-Ferraz, M. M., Almeida, M. F., Rivera-Utrilla, J., & Sanchez-Polo, M. Waste materials for activated carbon preparationand its use in aqueous -phase treatment: A review. *J. of Environmental Management* , 833-846. (2007).

[6]. El-Hendawy, AInfluence of HNO3 oxidation on the structure and adsorptive properties of corncob-based activated carbon. *Carbon* , 713-722. (2003).

[7]. Gratuito, M.K.B., Panyathanmaporn, T. and Chumnanklang, R.A., , "Production of Activated Carbon from Coconut Shell: Optimization using Response Surface Methodology," Bioresource Technology; Vol. 99, pp. 4887-4894.(2008)

[8]. Hu, Z., Srinivasan, M.P., Ni, Y., 2001. Novel activation process for preparing highly microporous and mesoporous activated carbons. Carbon 39, 877-886.

[9]. Inagaki, M., 2009. Pores in carbon materials-importance of their control. New Carbon Mater. 24 (3), 193-232.

[10]. Lillo-Rodenas, M. A., Marco-Lozar, J. P., Cazorla-Amoros, D., & Linares-Solano, A. (2007). Activated carbons prepared by pyrolysis of mixture of carbon precursor/alkaline hydroxide. *J. of Analytical and Applied Pyrolysis* , 166-174. (2003).

[11]. Mohan D., Kunwar, P. Singh and Vinod, K. Singh., , "Wastewater Treatment using Low Cost Activated

Carbons Derived from Agricultural by Products - ACase Study," Journal of Hazardous materials, Vol. 152, pp. 1045-1053. (2008).
[12]. Muller, B. R Effect of particle size and surface area on the adsorption of albumin-bonded bilirubin on activated carbon. Carbon Vol. 48, p. 3607-3615 (2010).
[13]. Omar, R., Idris, A., Yunus, R., Khalid, K., Isma. M.I, Characterisation of empty fruit bunch for microwave-assisted pyrolysis, Fuel 90, 1536-1544. (2011).
[14]. Quartey, E. T., and Chylkova, J. Challenges and Opportunities in managing agricultural waste in Ghana. Advances in Environment, Biotechnology and Biomedicine, pp:235-239, (2013).
[15]. Selomulya, C., Mee yoo, V., & Amal, R. Mechanisms of Cr(VI) removal from water by various types of activated carbons. *J. of Chemical Technol. and Biotechnology* , 74:111-122. (1999).
[16]. Shalaby, .C.S. L. Artok and C. Sarici: Preparation and characterization of activated carbons by one-step steam pyrolysis/activation from apricot stones. Microporous and mesoporous materials Vol. 88, p. 126-134, (2006).
[17]. Tsamba, A. J, Weihong Yang. and Wlodzimierz Blasia., , "Pyrolysis Characteristics and Global Kinetics of Coconut and Cashew Nut Shells," Fuel Processing Technology, Vol. 87, pp. 523-550.(2006)
[18]. Wel Su, Li Z. and Yapping, Z., , "Preparation of Micro Porous Activated Carbon from Raw Coconut Shell by Two-Step Procedure," Chinese Journal of Chemical Engineering, Vol. 14, pp. 266-269. (2006)
[19]. Yeganeh, M. M., Kaghazchi, T., & Soleimani, M. Effect of Raw Materials on Properties of Activated carbons. *Chem. Eng. Technol.* , 1247-1251.(2006).
[20]. Yun Ju Hwang, Jeong, S.K. and Shin, J.S., "High Capacity Disordered Carbons obtained from Coconut Shells as Anode Materials for Lithium Batteries," Journal of Alloys and Compounds, Vol. 448, pp. 141-147.(2008).